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CITATION:

Kim, Kyoung-Kook ...[et al]. High electron concentration and mobility in Al-doped n-ZnO epilayer achieved via dopant activation using rapid-thermal annealing. JOURNAL OF APPLIED PHYSICS 2005, 97(6): 066103.

ISSUE DATE:

2005-03-15

URL:

http://hdl.handle.net/2433/39711

JOURNAL OF APPLIED PHYSICS **97**, 066103 (2005)

High electron concentration and mobility in Al-doped *n*-ZnO epilayer achieved via dopant activation using rapid-thermal annealing

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(Received 8 November 2004; accepted 11 January 2005; published online 11 March 2005)

We report on the growth of very high-quality Al-doped *n*-type ZnO epilayers on sapphire substrates using a radio-frequency (rf) magnetron sputtering technique combined with a rapid-thermal annealing. Photoluminescence (PL) and Hall measurements show that both the optical and electrical properties of the ZnO layers are significantly improved with an increasing annealing temperature up to 900 °C. For example, the samples that are grown at 600 °C and a rf power of 100 W with an Ar/O_2 gas ratio of 1 give an electron concentration of 1.83×10^{20} cm^3 and a mobility of 65.6 $cm^2/V\,s$, when annealed at 900 °C for 3 min in a nitrogen ambient. Furthermore, x-ray diffraction measurements show that both the as-grown and annealed samples are of excellent crystallinity. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1863416]

Zinc oxide (ZnO) is a wide-band-gap (3.37 eV) semiconductor at room temperature and possesses a low threshold for optical pumping, a large exciton binding energy of 60 meV, the availability of a ZnO substrate, and the possibility of high doping. These unique characteristics make ZnO films very useful in excitonic-related optoelectronic device applications, such as ultraviolet light-emitting diodes (LEDs) and laser diodes (LDs). So far, in order to grow high-quality ZnO layers, different deposition techniques, such as molecular-beam epitaxy, pulsed laser deposition, metal-organic chemical-vapor deposition, and radio-frequency (rf) magnetron sputtering, have been developed. In addition, device processing, such as ohmic contact[1] and dry etching,[2] have been studied. In particular, since the successful growth of *p*-type ZnO films, the possibility for the realization of ZnO-based optoelectronic devices has been demonstrated.[3–5] Despite the progress in the growth of ZnO layers, however, the optical and electrical properties of *n*-ZnO layers are still not sufficiently good enough for the realization of high efficiency devices. In our recent work on the growth of phosphorous (P)-doped *p*-ZnO layers, it was shown that the post-deposition rapid-thermal annealing (RTA) treatment is very effective in improving their electrical and optical properties.[3] In this article, we have investigated the formation of high-quality Al-doped *n*-ZnO (*n*-ZnO:Al) layers on (0001) sapphire substrates by RTA treatment and rf magnetron sputtering method, which enables the growth of large area films and the easy control of layer compositions.[6,7] It is shown that annealing the samples at 900 °C for 3 min in a nitrogen ambient results in an electron mobility of 65.6 $cm^2/V\,s$ and a carrier concentration of 1.83×10^{20} cm^3.

The *n*-ZnO:Al layers (with a thickness of 1 μm) were grown on (0001) *c*-plane sapphire substrates by a rf magnetron sputtering system using an Al_2O_3 (2 wt %)-doped ZnO target (2 in. in diameter). The growth rate was 0.5 $\mu m/h$ and the substrate temperature was 600 °C. The working pressure in the growth chamber was kept fixed at 10 mTorr. The Ar/O_2 gas ratio and the rf power were varied from 1 to 4 and from 60 to 140 W, respectively. The as-grown samples were then rapid-thermal annealed (RTA) at temperatures in the range of 700–1000 °C for 3 min in a nitrogen ambient. During the RTA, the temperature ramping rate was kept at 25 °C/s. The Hall measurements were used to characterize the electrical properties of the *n*-ZnO layers. The structural and optical properties of the *n*-ZnO layers were examined by high-resolution x-ray diffraction (XRD) and photoluminescence (PL) spectroscopy [using a He–Cd laser ($\lambda=325$ nm) as an excitation source at room temperature].

Figure 1 shows the annealing temperature dependence of the electrical properties of the samples that were grown at a rf power of 100 W with an Ar/O_2 gas ratio of 1. It is shown that as the annealing temperature increases up to 1000 °C, both the electron concentration and mobility increase, reach a maximum at 900 °C and then decrease. It is found that annealing the samples at 900 °C yields the best electrical property. In addition, it is thought that the electrical proper-

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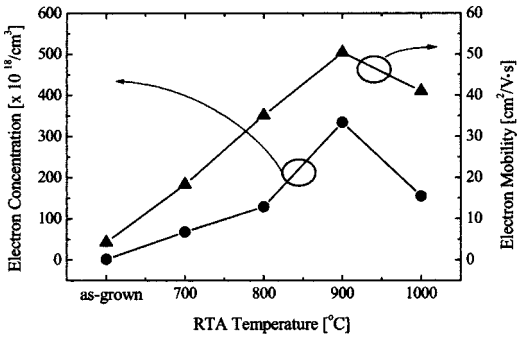

FIG. 1. The annealing temperature dependence of the electrical properties of the samples that were grown at 600 °C and a rf power of 100 W with an Ar/O_2 gas ratio of 1.

ties are degraded due to the out diffusion of the dopants or the decomposition of the films induced by a high thermal energy during the annealing at a high temperature of above 900 °C.

Figure 2(a) shows the annealing temperature dependence of the PL spectra of the samples that were grown at 100 W with a gas ratio of 1. The as-grown sample shows a fairly weak PL peak. However, as the annealing temperature increases up to 900 °C, the PL intensity is increased significantly. (It should be noted that regardless of the growth conditions, annealing the samples at 900 °C always results in similar PL intensities of the near-band-edge emission peaks.) A further increase in the temperature up to 1000 °C leads to the decrease of the PL intensity. However, the deep level emission is not observed in the PL spectra of the 1000 °C-annealed sample. This PL behavior is similar to the temperature dependence of the electrical property of the samples (Fig. 1).

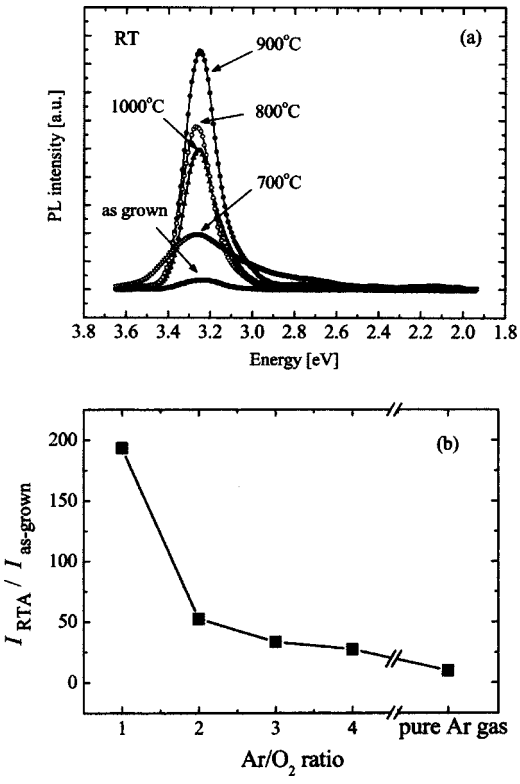

FIG. 2. (a) The annealing temperature dependence of the PL spectra of the samples that were grown at 600 °C and 100 W with a gas ratio of 1. (b) The PL intensity ratio ($I_{RTA}/I_{as\text{-}grown}$) of the band-edge peaks of the samples (that were grown at 600 °C and 100 W) as a function of the Ar/O_2 gas ratio.

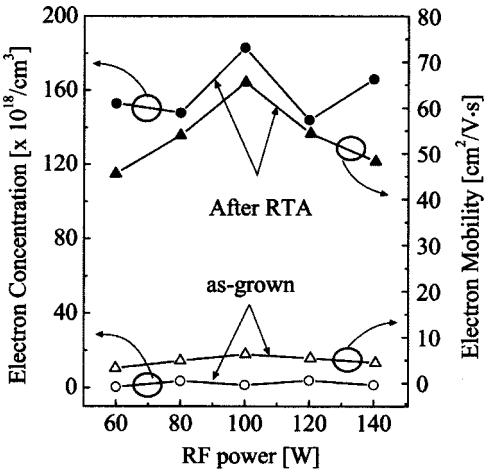

FIG. 3. The rf power dependence of the electrical properties of the samples (that were grown at 600 °C with a gas ratio of 1) before and after annealing at 900 °C.

Figure 2(b) shows the PL intensity ratio ($I_{RTA}/I_{as\text{-}grown}$) of the near-band-edge peaks of the samples (after and before annealing at 900 °C, respectively) as a function of the Ar/O_2 gas ratio. For comparison, a sample was also grown in a pure Ar gas ambient at the same conditions. It is shown that the PL intensity ratio is considerably enhanced with increasing oxygen partial pressure. This indicates that $I_{as\text{-}grown}$ decreases significantly with increasing oxygen partial pressure, since I_{RTA} is almost the same in all samples annealed at 900 °C. In other words, the PL property of the as-grown samples becomes degraded with increasing oxygen partial pressure. This behavior could be related to the generation of defectlike Al oxides, which act as nonradiative emission centers. As the oxygen content is increased, the formation of the Al oxides is not only facilitated, but the amount of the Al oxides is also increased. Thus, the PL property of the samples is degraded with increasing oxygen content.

Figure 3 shows the rf power dependence of the electrical properties of the samples (that were grown at an Ar/O_2 gas ratio of 1) before and after annealing. It is shown that for the as-grown samples, their electrical properties are almost independent of the rf powers. Measurements show that the electron concentrations and mobilities are of the order of 10^{18} cm^3 and less than 8 cm^2/V s, respectively. When annealed at 900 °C, however, the samples produce remarkably improved carrier concentrations and mobilities, e.g., about 10^{20} cm^3 and 45–65 cm^2/V s, respectively. These are among the best values reported so far for the *n*-ZnO layers.[8,9] It is worth noting that the sample grown at 100 W gives the highest electron concentration and mobility.

In addition, the in-plane alignment of the as-grown ZnO layers (that were grown at 600 °C and 100 W with a gas ratio of 1) was measured using the phi scan of the four-circle XRD to characterize their structural properties (not shown). The results showed that the $(01\bar{1}2)$ plane of the ZnO layers has the sixfold symmetry, showing the in-plane epitaxial re-

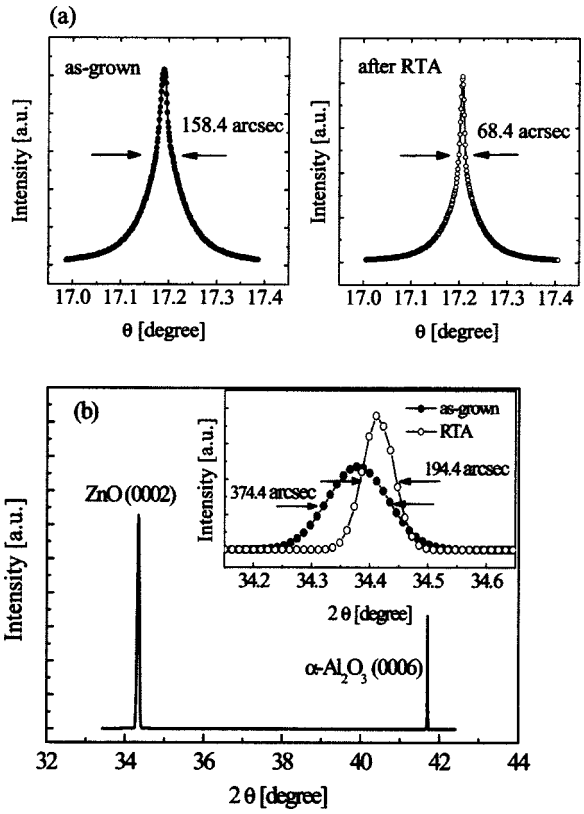

FIG. 4. (a) The θ-rocking curves of the ZnO layers (that were grown at 600 °C and 100 W with a gas ratio of 1) before and after annealing at 900 °C. (b) XRD θ-2θ scan profiles from the as-grown samples (that were grown at 600 °C and 100 W with a gas ratio of 1).

lationship of ZnO $[10\bar{1}0]\|\alpha$-$Al_2O_3[11\bar{2}0]$.[7] Figure 4(a) shows the Θ-rocking curves of the ZnO layers before and after annealing at 900 °C. The full width at half maximum (FWHM) of the as-grown and annealed samples was measured to be 158.4 and 68.4 arc sec, respectively. Compared with the ZnO films grown by various other growth techniques,[8–10] these results indicate the ZnO films of high-quality crystallinity. It is noted that even the as-grown sample itself is of excellent crystallinity. Figure 4(b) shows the XRD θ-2θ scan profiles from the as-grown samples. Irrespective of the RTA process, only the (0002) diffraction peak was observed. It is shown that the (0002) peak slightly shifts toward the high angle side by 0.03° upon annealing at 900 °C. It is also shown that annealing causes an increase of the (0002) peak intensity by a factor of 1.5. Furthermore, the FWHM of the θ-2θ scan curves became narrower by 180 arc sec when annealed. These results indicate that the compressive strain builtup in the as-grown samples is relaxed by the postgrowth annealing processes.[11]

Although the as-grown ZnO layer was of excellent crystallinity (Fig. 4), its PL property was pretty poor, as shown in Fig. 2. This implies that the as-grown sample contains defect-related nonradiative emission centers. Thermodynamic calculations show that the free energy of the formation (ΔG_f) of Al_2O_3 is −1582.3 kJ/mol, which is lower than that of ZnO (ΔG_f=−320.5 kJ/mol).[12] In addition, the bonding strength of Al–O and Zn–O are 511±3 and 159±4 kJ/mol, respectively.[12] Thus, the comparison of the formation free energies and bonding strengths indicates that Al oxides,[13,14] such as Al_2O_3 and/or Al_xO_y, could be easily formed and as a result incorporated in ZnO during growth. Thus, the presence of such defectlike Al oxides could be responsible for the poor PL property of the as-grown samples. However, when the samples are rapid-thermal annealed, the Al oxides are activated (decomposed), which generates Al donors and so leads to the increase in the carrier concentration (and hence the improvement of their PL properties). Because such activation process of the Al oxides acted to defects in films decreases density of defects with increase of electron concentration, the mean free path of electron is increased in annealed *n*-ZnO:Al films. As the results of activation, the electron mobility is increased with concentration of electrons, as shown in Fig. 1. Such annealing behavior was also observed in phosphorous (P)-doped *p*-type ZnO, where P oxides are activated as acceptors by the RTA process.[3]

In summary, we investigated the growth of a high-quality Al-doped *n*-ZnO layer on sapphire substrates by a rf magnetron sputtering technique combined with a RTA process. It was shown that annealing the as-grown samples at 900 °C for 3 min in a nitrogen atmosphere results in a very high-quality *n*-ZnO. For example, the samples that were grown at 600 °C and a rf power of 100 W with an Ar/O_2 gas ratio of 1 yielded a carrier concentration of 1.83×10^{20} cm^3 and a mobility of 65.6 cm^2/V s. In addition, the FWHM of XRD θ-rocking curve of the as-grown and annealed samples is 158.4 and 68.4 arc sec, respectively. The annealing-induced improvements of the electrical and optical properties of the samples were explained in terms of the activation of Al oxides by RTA.

This work was partially supported by National Research Laboratory Program in Korea.

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